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Synthesis of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives via $ZnCl_2$ catalyzed cyclocondensation reaction

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Abstract—A short and facile synthesis of a series of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives was accomplished in moderate to good yields via the novel cyclocondensation of substituted *o*-aminobenzonitrile with aldehydes or ketones catalyzed by $ZnCl_2$.

1. Introduction

A literature survey of important and valuable physiological properties for 1,2-dihydro-4*H*-3,1-benzoxazine derivatives includes nonsteroidal progesterone receptor agonists,[1,2] plant growth regulating, and herbicide activities.[3] In addition, these compounds can be transformed into their 4*H*-3,1-benzoxazine analogues,[4] which also include important pharmacologically active compounds.[5,6]

The main synthetic approach to 1,2-dihydro-4*H*-3,1-benzoxazines is the condensation of *o*-aminobenzyl alcohols with carbonyl compounds.[7,8] However, limitations related to difficulty in obtaining these benzyl alcohols have prevented the use of these reactions for the synthesis of 1,2-dihydro-4*H*-3,1-benzoxazines. Here, we wish to describe a new method for the preparation of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives using substituted *o*-aminobenzonitrile as the starting material in DMF catalyzed by $ZnCl_2$.[9]

2. Results and discussion

2.1. Choice of catalyst

The choice of the catalyst played a crucial role and the use of $ZnCl_2$ was at the center of our study. In the course of our work on applications of $ZnCl_2$ in organic reactions, we have found that it is an effective catalyst for the preparation of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives. The use of anhydrous $AlCl_3$, CuCl, $CuCl_2$, $TiCl_4$, and *p*-toluenesulfonic was much less effective. When a mixture of 2-amino-5-nitrobenzonitrile **1a** and cyclohexanone **2** in DMF was stirred under reflux in the presence of $ZnCl_2$, the reaction was completed within 1 h. After work up, the product **3a** was obtained in 75% yield (Table 1). In contrast to the above result, we carried out the reaction of **1a** with **2** in the presence of anhydrous $AlCl_3$. However, the product **3a** was not obtained. After screening several Lewis acids, we found that $ZnCl_2$ was the best catalyst for the reaction of 2-amino-5-nitrobenzonitrile **1a** and cyclohexanone **2** (Table 1).

2.2. Synthesis of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives

Then, we studied the reaction of differently substituted *o*-aminobenzonitrile with cyclohexanone. Thus, treatment of a solution of 2-amino-4-chlorobenzonitrile with cyclohexanone in the presence of $ZnCl_2$ in DMF at reflux for 2 h afforded 1,2-dihydro-4*H*-3,1-benzoxazines **3b** in 70% yield (Table 2). The same treatment of *o*-aminobenzonitrile with cyclohexanone gave the cyclocondensation product **3c** in 64% yield. Similarly, when cyclopentanone was used instead of cyclohexanone, 1,2-dihydro-4*H*-3,1-benzoxazines were also obtained. The optimized results are summarized in Table 2.

Encouraged by this study, we investigated the reaction of differently substituted *o*-aminobenzonitrile **1** with a range of aliphatic ketones, aldehydes, or aromatic aldehydes **4** bearing either electron-donating or electron-withdrawing substitutes, affording moderate to good yields of products 1,2-dihydro-4*H*-3,1-benzoxazine derivatives **5**. The optimized results are summarized in Table 3.

Keywords: $ZnCl_2$; Cyclocondensation; 1,2-Dihydro-4*H*-3,1-benzoxazine derivatives; Aldehydes; Ketones.
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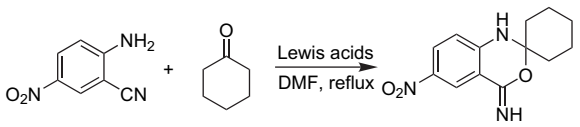
Table 1. Screening of Lewis acids[a,b]

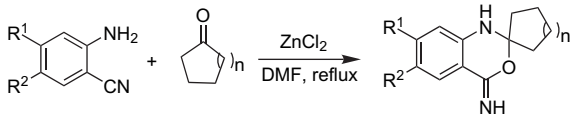


1a **2** **3a**

Entry	LA	Time (h)	Yield (%)[c]
1	$AlCl_3$	1	0
2	CuCl	1	38
3	$CuCl_2$	1	32
4	$TiCl_4$	1	0
5	$ZnCl_2$	1	75
6	p-$CH_3C_6H_4SO_3H$	1	13

[a] Yields of **3a** using different LAs in the reaction of 2-amino-5-nitrobenzonitrile and cyclohexanone.
[b] All reactions were carried out using **1a** (6 mmol), **2** (4 mL), LAs (6 mmol), and DMF (8 mL).
[c] Isolated yield.

Table 2. The cyclocondensation of substituted *o*-aminobenzonitrile and cyclic ketones[a]



1 **2** **3**

Entry	R^1	R^2	n	Time (h)	Product	Yield (%)[b]
1	H	NO_2	2	1	**3a**	75
2	Cl	H	2	1.5	**3b**	70
3	H	H	2	2.5	**3c**	64
4	H	NO_2	1	1	**3d**	70
5	Cl	H	1	2	**3e**	67
6	H	H	1	2.5	**3f**	62

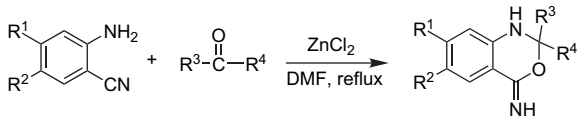
[a] All reactions were carried out using **1** (6 mmol), **2** (4 mL), $ZnCl_2$ (6 mmol), and DMF (8 mL).
[b] Isolated yield.

As shown in Table 3, various ketones or aldehydes reacted with substituted *o*-aminobenzonitrile in the presence of $ZnCl_2$ affording the desired 1,2-dihydro-4*H*-3,1-benzoxazine derivatives in moderate to good yields. When 2-amino-4-chlorobenzonitrile was used instead of 2-amino-5-nitrobenzonitrile for the reaction, the yields of **5d–f** and **5p–u** were lower than that of **5a–c** and **5j–o**. Moreover, when *o*-aminobenzonitrile reacted with various ketones or aldehydes, the yields of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives were lower. So, the yields seemed to depend on the substituted groups in *o*-aminobenzonitrile. The reaction proceeded more readily and gave better yields if the *o*-aminobenzonitrile derivatives possessed stronger electron-withdrawing substituent.

2.3. Mechanism

The formation of products 1,2-dihydro-4*H*-3,1-benzoxazine derivatives can be explained by Scheme 1. The attack of the amino group of **1** onto the carbonyl carbon atom of **4** gave intermediate **6** and the product **5** was obtained through subsequent cyclization by attack of the oxygen atom onto the nitrile group of **1**.

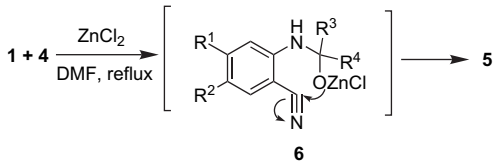
Table 3. The synthesis of 1,2-dihydro-4*H*-3,1-benzoxazines catalyzed by $ZnCl_2$



1 **4** **5**

Entry	R^1	R^2	R^3	R^4	Time (h)	Product	Yield (%)[a]
1	H	NO_2	CH_3	CH_3	1	**5a**	82
2	H	NO_2	CH_3CH_2	CH_3	1	**5b**	80
3	H	NO_2	C_6H_5	CH_3	2	**5c**	78
4	Cl	H	CH_3	CH_3	1.5	**5d**	71
5	Cl	H	CH_3CH_2	CH_3	1.5	**5e**	74
6	Cl	H	C_6H_5	CH_3	2.5	**5f**	70
7	H	H	CH_3	CH_3	2.5	**5g**	65
8	H	H	CH_3CH_2	CH_3	2.5	**5h**	67
9	H	H	C_6H_5	CH_3	3	**5i**	62
10	H	NO_2	$CH_3CH_2CH_2$	H	1	**5j**	75
11	H	NO_2	C_6H_5	H	1	**5k**	80
12	H	NO_2	m-$O_2NC_6H_4$	H	1	**5l**	80
13	H	NO_2	p-$O_2NC_6H_4$	H	1	**5m**	71
14	H	NO_2	p-$CH_3OC_6H_4$	H	1	**5n**	82
15	H	NO_2	p-ClC_6H_4	H	1	**5o**	80
16	Cl	H	$CH_3CH_2CH_2$	H	2	**5p**	72
17	Cl	H	C_6H_5	H	2	**5q**	75
18	Cl	H	m-$O_2NC_6H_4$	H	2	**5r**	78
19	Cl	H	p-$O_2NC_6H_4$	H	2	**5s**	70
20	Cl	H	p-$CH_3OC_6H_4$	H	2	**5t**	76
21	Cl	H	p-ClC_6H_4	H	2	**5u**	75
22	H	H	$CH_3CH_2CH_2$	H	2.5	**5v**	60
23	H	H	C_6H_5	H	2.5	**5w**	71
24	H	H	m-$O_2NC_6H_4$	H	2.5	**5x**	73
25	H	H	p-$O_2NC_6H_4$	H	2.5	**5y**	67
26	H	H	p-$CH_3OC_6H_4$	H	2.5	**5z**	73
27	H	H	p-ClC_6H_4	H	2.5	**5aa**	70

[a] Isolated yield.



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Scheme 1. Proposed mechanism.

2.4. Crystallographic structure of compound 3d

The structure of the products was further confirmed by X-ray crystallographic analysis of **3d**. Crystals of **3d** was obtained by recrystallization from ethanol. Molecular structure and the crystal packing of **3d** are shown in Figure 1. The structure showed cyclopentane rings with an envelope conformation. The C1–N2 bond (1.238 Å) possessing double bond character was significantly shorter than the C8–N1 bond (1.463 Å). The tight crystal packing with significant N1–H···O3 (2.996 Å) and N2–H···O1 (2.896 Å) hydrogen bonds in the structure was in agreement with the observed high melting point.

3. Conclusion

In conclusion, we have described a novel method for the efficient and convenient synthesis of 1,2-dihydro-4*H*-3,1-

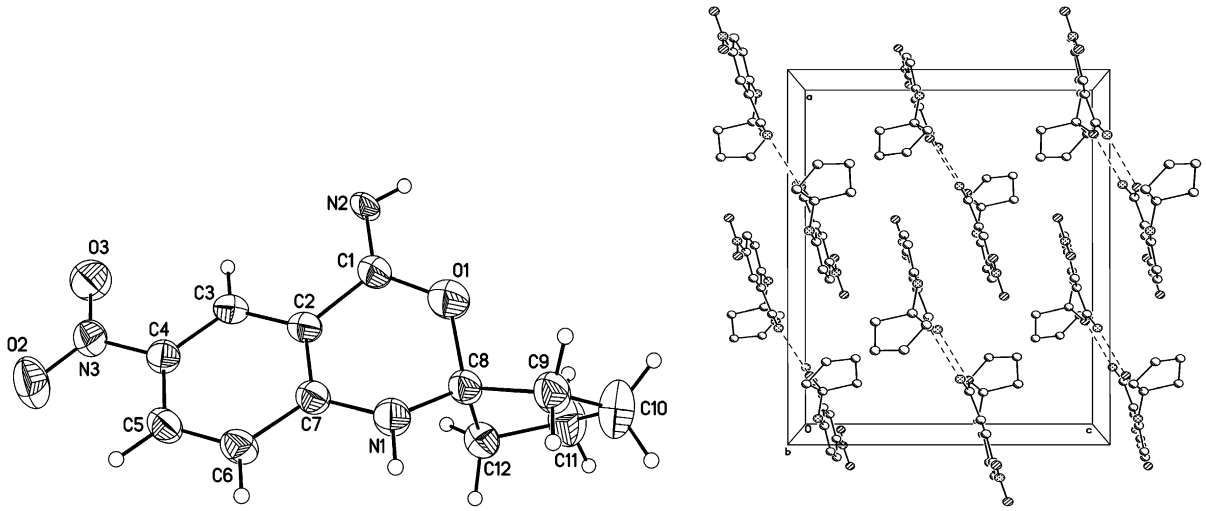

Figure 1. Crystal structure and packing diagram of compound **3d**.

benzoxazine derivatives via cyclocondensation of substituted *o*-aminobenzonitrile and aldehydes or ketones using the easily available $ZnCl_2$ as catalyst in DMF. The advantages of our method are the easily accessible starting materials, facile experimental work up procedure, and moderate to good yields.

4. Experimental

4.1. General

Melting points were determined using XT4 microscope melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin Elmer FT-IR spectrophotometer and were run as KBr pellets. ^1H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker 400 spectrometer. Chemical shifts were reported in δ (ppm) relative to internal tetramethylsilane. Mass spectra were recorded on a ZAB-HS mass spectrometer using ESI ionization. Elemental analyses were within ±0.4% of theoretical values and were performed on an Elementar Vario EL.

4.1.1. Typical procedure for the preparation of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives (3a–f, 5a–i). To a solution of DMF (8 mL) and $ZnCl_2$ (6 mmol) were added substituted *o*-aminobenzonitrile **1** (6 mmol) and ketones (4 mL). The mixture was heated at reflux for the specified time (see Tables 2 and 3). After completion of the reaction as indicated by TLC (eluent: ethyl acetate), the cooled reaction mixture was quenched with water (10 mL) and the precipitate was separated by filtration. The filtration residue was dispersed into water and titrated to pH 12–13 by 20% sodium hydroxide. After filtration, the product was isolated by column chromatography (200–300 mesh silica gel, ethyl acetate–petroleum=1:2).

4.1.1.1. 6-Nitro-1,2-dihydro-2,2-(1′,5′-pentylene)-4-imino-4*H*-3,1-benzoxazine (3a). Yellow solid. Mp 297–299 °C. IR (KBr): 3359, 3188, 2935, 1672, 1618, 1529, 1313 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.05–1.80 (10H, m, C_5H_{10}), 6.94 (1H, d, J=7.7 Hz, ArH), 8.08 (1H, s, NH), 8.10 (1H, dd, J=2.8, 7.7 Hz, ArH), 8.39 (1H, d, J=2.8 Hz, ArH), 8.44 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 21.13 (2C), 24.74, 38.36 (2C), 69.19, 112.88, 114.99, 124.57, 129.26, 137.27, 151.85, 161.66; MS (ESI): m/z (%)=262.2 (100) $[M+H]^+$; $C_{13}H_{15}N_3O_3$: calcd C 59.76, H 5.78, N 16.08; found C 59.73, H 5.79, N 16.09.

4.1.1.2. 7-Chloro-1,2-dihydro-2,2-(1′,5′-pentylene)-4-imino-4*H*-3,1-benzoxazine (3b). Pale yellow solid. Mp 220–221 °C. IR (KBr): 3320, 3176, 2920, 1641, 1607, 1476 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.25–1.78 (10H, m, C_5H_{10}), 6.63 (1H, dd, J=8.0, 2.0 Hz, ArH), 6.87 (1H, d, J=2.0 Hz, ArH), 6.91 (1H, s, NH), 7.55 (1H, d, J=8.0 Hz, ArH), 8.06 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 20.83 (2C), 24.48, 37.22 (2C), 68.14, 113.17, 113.60, 116.40, 129.07, 137.60, 147.71, 162.29; MS (ESI): m/z (%)=251.1 (100) $[M+H]^+$; $C_{13}H_{15}N_2OCl$: calcd C 62.27, H 6.03, N 11.17; found C 62.14, H 6.16, N 10.96.

4.1.1.3. 1,2-Dihydro-2,2-(1′,5′-pentylene)-4-imino-4*H*-3,1-benzoxazine (3c). White solid. Mp 231–233 °C. IR (KBr): 3365, 3170, 2923, 1648, 1610, 1504, 1484, 1382 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.23–1.74 (10H, m, C_5H_{10}), 6.60 (1H, d, J=8.0 Hz, ArH), 6.63 (1H, s, NH), 6.79 (1H, d, J=8.0 Hz, ArH), 7.20 (1H, t, J=8.0 Hz, ArH), 7.56 (1H, t, J=8.0 Hz, ArH), 7.89 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 20.84 (2C), 24.61, 37.12 (2C), 67.76, 114.42, 114.53, 116.43, 127.05, 133.07, 146.72, 163.14; MS (ESI): m/z (%)=217.1 (100) $[M+H]^+$; $C_{13}H_{16}N_2O$: calcd C 72.19, H 7.46, N 12.95; found C 71.88, H 7.44, N 12.82.

4.1.1.4. 6-Nitro-1,2-dihydro-2,2-(1′,4′-butylene)-4-imino-4*H*-3,1-benzoxazine (3d). Yellow solid. Mp 281–283 °C. IR (KBr): 3319, 3180, 2912, 1672, 1619, 1534, 1310 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.67–1.88 (8H, m, C_4H_8), 6.82 (1H, d, J=8.0 Hz, ArH), 8.10 (1H, dd, J=2.4, 8.0 Hz, ArH), 8.30 (1H, s, NH), 8.42 (1H, d, J=2.4 Hz, ArH), 8.56 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 21.90 (2C), 40.15 (2C), 77.32, 112.31, 114.14, 124.11, 128.62, 136.68, 151.63, 161.21; MS (ESI): m/z (%)=248.2 (100) $[M+H]^+$; $C_{12}H_{13}N_3O_3$: calcd C 58.29, H 5.30, N 17.00; found C 58.33, H 5.31, N 17.08.

4.1.1.5. 7-Chloro-1,2-dihydro-2,2-(1′,4′-butylene)-4-imino-4*H*-3,1-benzoxazine (3e). Pale yellow solid. Mp 250–251 °C. IR (KBr): 3310, 3181, 2942, 1648, 1608, 1481 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.66–1.80 (8H, m, C_4H_8), 6.64 (1H, dd, J=8.0, 2.0 Hz, ArH), 6.73 (1H, d, J=2.0 Hz, ArH), 7.04 (1H, s, NH), 7.56 (1H, d, J=8.0 Hz, ArH), 8.21 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 20.91 (2C), 38.96 (2C), 72.10, 113.02, 113.21, 116.12, 129.01, 136.92, 147.15, 162.01; MS (ESI): m/z (%)=237.1 (100) $[M+H]^+$; $C_{12}H_{13}N_2OCl$: calcd C 60.89, H 5.53, N 11.83; found C 60.51, H 5.46, N 11.48.

4.1.1.6. 1,2-Dihydro-2,2-(1′,4′-butylene)-4-imino-4*H*-3,1-benzoxazine (3f). White solid. Mp 268–270 °C. IR (KBr): 3289, 3166, 2934, 1638, 1613, 1429 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.75–2.08 (8H, m, C_4H_8), 6.07 (1H, s, NH), 6.73 (2H, dd, J=7.8, 8.0 Hz, ArH), 7.19 (1H, s, =NH), 7.24–7.26 (1H, m, J=7.2 Hz, ArH), 7.73 (1H, d, J=8.0 Hz, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 21.97 (2C), 38.88 (2C), 77.05, 114.32, 114.57, 116.53, 127.23, 132.99, 147.49, 163.42; MS (ESI): m/z (%)=203.1 (100) $[M+H]^+$; $C_{12}H_{14}N_2O$: calcd C 71.26, H 6.98, N 13.85; found C 71.38, H 6.71, N 13.49.

4.1.1.7. 6-Nitro-1,2-dihydro-2,2-dimethyl-4-imino-4*H*-3,1-benzoxazine (5a). Yellow solid. Mp 291–293 °C. IR (KBr): 3322, 3177, 1671, 1618, 1534, 1306, 1149 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.45 (6H, s, CH_3), 6.74 (1H, d, J=8.8 Hz, ArH), 8.09 (1H, dd, J=2.7, 8.8 Hz, ArH), 8.24 (1H, s, NH), 8.41 (1H, d, J=2.7 Hz, ArH), 8.56 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 29.68 (2C), 67.57, 111.70, 114.09, 124.15, 128.85, 136.68, 151.33, 160.87; MS (ESI): m/z (%)=222.1 (100) $[M+H]^+$; $C_{10}H_{11}N_3O_3$: calcd C 54.29, H 5.01, N 18.99; found C 54.41, H 5.12, N 18.78.

4.1.1.8. 6-Nitro-1,2-dihydro-2-methyl-2-ethyl-4-imino-4*H*-3,1-benzoxazine (5b). Yellow solid. Mp 283–285 °C. IR (KBr): 3322, 3177, 2919, 1671, 1618, 1534, 1306, 1149 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.88 (3H, t, J=7.2 Hz, CH_3), 1.43 (3H, s, CH_3), 1.64–1.73 (2H, m, J=7.2 Hz, CH_2), 6.75 (1H, d, J=8.8 Hz, ArH), 8.08 (1H, dd, J=2.7, 8.8 Hz, ArH), 8.17 (1H, s, NH), 8.36 (1H, s, =NH), 8.40 (1H, d, J=2.7 Hz, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 7.93, 28.57, 34.99, 70.29, 111.42, 113.75, 124.12, 128.90, 136.39, 151.78, 161.01; MS (ESI): m/z (%)=236.1 (100) $[M+H]^+$; $C_{11}H_{13}N_3O_3$: calcd C 56.16, H 5.57, N 17.86; found C 55.98, H 5.67, N 17.48.

4.1.1.9. 6-Nitro-1,2-dihydro-2-methyl-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5c). Yellow solid. Mp 329–331 °C. IR (KBr): 3352, 3188, 1674, 1617, 1535, 1310, 1150 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.74 (3H, s, CH_3), 6.89 (1H, d, J=8.8 Hz, ArH), 7.24 (1H, t, J=7.2 Hz, ArH), 7.34 (2H, t, J=7.2, 8.0 Hz, ArH), 7.47 (2H, d, J=8.0 Hz, ArH), 8.10 (1H, dd, J=2.7, 8.8 Hz, ArH), 8.33 (1H, d, J=2.7 Hz, ArH), 9.02 (1H, s, NH), 9.22 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 30.14, 70.50, 113.00, 114.44, 124.05, 124.79 (2C), 127.61, 128.33 (2C), 128.93, 137.22, 146.64, 151.55, 161.82; MS (ESI): m/z (%)=284.1 (100) $[M+H]^+$; $C_{15}H_{13}N_3O_3$: calcd C 63.59, H 4.62, N 14.83; found C 63.42, H 4.75, N 14.96.

4.1.1.10. 7-Chloro-1,2-dihydro-2,2-dimethyl-4-imino-4*H*-3,1-benzoxazine (5d). Pale yellow powder. Mp 227–229 °C. IR (KBr): 3311, 2978, 1627, 1602 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.52 (6H, s, CH_3), 6.57 (1H, s, NH), 6.71 (1H, dd, J=2.0, 8.0 Hz, ArH), 6.80 (1H, d, J=2.0 Hz, ArH), 7.70 (1H, d, J=8.0 Hz, ArH), 8.16 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 29.45 (2C), 69.68, 111.32, 112.83, 116.15, 129.12, 137.83, 148.32, 162.34; MS (ESI): m/z (%)=211.1 (100) $[M+H]^+$; $C_{10}H_{11}N_2OCl$: calcd C 57.01, H 5.26, N 13.30; found C 57.37, H 5.33, N 13.18.

4.1.1.11. 7-Chloro-1,2-dihydro-2-methyl-2-ethyl-4-imino-4*H*-3,1-benzoxazine (5e). Pale yellow solid. Mp 174–176 °C. IR (KBr): 3297, 3188, 2971, 1640, 1606 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.86 (3H, t, J=7.2 Hz, CH_3), 1.36 (3H, s, CH_3), 1.57–1.67 (2H, m, J=7.2 Hz, CH_2), 6.60 (1H, dd, J=2.0, 8.0 Hz, ArH), 6.67 (1H, d, J=2.0 Hz, ArH), 6.89 (1H, s, NH), 7.54 (1H, d, J=8.0 Hz, ArH), 8.00 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 8.12, 27.59, 34.09, 69.63, 111.28, 112.91, 115.96, 129.06, 137.64, 148.18, 162.24; MS (ESI): m/z (%)=225.1 (100) $[M+H]^+$; $C_{11}H_{13}N_2OCl$: calcd C 58.80, H 5.83, N 12.47; found C 59.12, H 5.99, N 12.28.

4.1.1.12. 7-Chloro-1,2-dihydro-2-methyl-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5f). Pale yellow solid. Mp 106–107 °C. IR (KBr): 3318, 3181, 1668, 1606 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.65 (3H, s, CH_3), 6.60 (1H, dd, J=1.8, 8.0 Hz, ArH), 6.80 (1H, d, J=1.8 Hz, ArH), 7.20 (1H, t, J=7.2 Hz, ArH), 7.31 (2H, t, J=7.2, 8.0 Hz, ArH), 7.47 (3H, d, J=8.0 Hz, ArH), 7.92 (1H, s, NH), 8.90 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 30.51, 70.34, 113.31, 113.75, 116.85, 124.99 (2C), 127.19, 128.08 (2C), 129.21, 137.70, 147.19, 148.09, 162.91; MS (ESI): m/z (%)=273.2 (100) $[M+H]^+$; $C_{15}H_{13}N_2OCl$: calcd C 66.05, H 4.80, N 10.27; found C 65.78, H 5.12, N 10.01.

4.1.1.13. 1,2-Dihydro-2,2-dimethyl-4-imino-4*H*-3,1-benzoxazine (5g). White solid. Mp 190–191 °C. IR (KBr): 3325, 3166, 1629, 1606, 1511 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.38 (6H, s, CH_3), 6.59 (1H, d, J=7.6 Hz, ArH), 6.62 (1H, s, NH), 6.64 (1H, d, J=1.6 Hz, ArH), 7.20–7.23 (1H, m, J=1.6, 1.2, 7.6 Hz, ArH), 7.57 (1H, dd, J=1.2, 7.6 Hz, ArH), 7.87 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 28.90 (2C), 66.73, 113.78, 114.13, 116.31, 127.06, 133.05, 146.96, 162.92; MS (ESI): m/z (%)=177.1 (100) $[M+H]^+$; $C_{10}H_{12}N_2O$: calcd C 68.16, H 6.86, N 15.90; found C 68.50, H 6.98, N 15.74.

4.1.1.14. 1,2-Dihydro-2-methyl-2-ethyl-4-imino-4*H*-3,1-benzoxazine (5h). White solid. Mp 153–155 °C. IR (KBr): 3340, 2913, 1631, 1609, 1540 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.72 (3H, t, J=6.8 Hz, CH_3), 1.15 (3H, s, CH_3), 1.70–1.76 (2H, m, CH_2), 6.16 (1H, s, NH), 6.55–6.59 (1H, m, J=8.0 Hz, ArH), 6.63 (1H, d, J=8.0 Hz, ArH), 7.18–7.22 (1H, m, J=1.2, 8.0 Hz, ArH), 7.61 (1H, dd, J=1.2, 8.0 Hz, ArH), 8.11 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 8.35, 27.37, 34.88, 71.59, 112.35, 115.51, 118.16, 128.72, 136.16, 148.57, 167.68; MS (ESI): m/z (%)=191.1 (100) $[M+H]^+$; $C_{11}H_{14}N_2O$: calcd C 69.45, H 7.42, N 14.73; found C 69.23, H 7.71, N 14.58.

4.1.1.15. 1,2-Dihydro-2-methyl-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5i). White solid. Mp 232–234 °C. IR (KBr): 3389, 3181, 1663, 1613 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 1.79 (3H, s, CH_3), 6.63–6.67 (1H, m, J=0.8, 8.0 Hz, ArH), 6.83 (1H, t, J=0.8, 8.0 Hz, ArH), 6.89 (1H, s, NH), 7.21–7.23 (2H, m, ArH), 7.28–7.32 (2H, m, ArH), 7.61–7.68 (3H, m, ArH), 7.93 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 31.14, 71.54, 115.36, 116.67, 118.26, 126.09 (2C), 128.00, 128.45, 128.87 (2C), 134.05, 147.95, 148.23, 164.90; MS (ESI): m/z (%)=239.1 (100) $[M+H]^+$; $C_{15}H_{14}N_2O$: calcd C 75.61, H 5.92, N 11.76; found C 75.28, H 6.11, N 11.43.

4.1.2. Typical procedure for the preparation of 1,2-dihydro-4*H*-3,1-benzoxazine derivatives (5j–aa). To a solution of DMF (10 mL) and $ZnCl_2$ (6 mmol) were added substituted *o*-aminobenzonitrile **1** (6 mmol) and aldehydes (8.4 mmol). The mixture was heated at reflux for the specified time (see Table 3). After completion of the reaction as indicated by TLC (eluent: ethyl acetate), the cooled reaction mixture was quenched with water (10 mL) and the precipitate was separated by filtration. The filtration residue was dispersed into water and titrated to pH 12–13 by 20% sodium hydroxide. After filtration, the product was isolated by column chromatography (200–300 mesh silica gel, ethyl acetate–petroleum=1:2).

4.1.2.1. 6-Nitro-1,2-dihydro-2-propyl-4-imino-4*H*-3,1-benzoxazine (5j). Yellow powder. Mp 235–237 °C. IR (KBr): 3362, 3190, 2927, 1689, 1623, 1515, 1450, 1324, 1302 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.90 (3H, t, J=7.2 Hz, CH_3), 1.38–1.42 (2H, m, CH_2), 1.61–1.67 (2H, m, CH_2), 4.94 (1H, t, J=5.0 Hz, CH), 6.80 (1H, d, J=8.8 Hz, ArH), 8.08 (1H, dd, J=2.7, 8.8 Hz, ArH), 8.13 (1H, s, NH), 8.36 (1H, s, =NH), 8.39 (1H, d, J=2.7 Hz, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 13.66, 16.21, 38.18, 63.94, 112.64, 114.12, 124.19, 128.76, 136.76, 152.76, 161.57; MS (ESI): m/z (%)=236.1 (100) $[M+H]^+$; $C_{11}H_{13}N_3O_3$: calcd C 56.16, H 5.57, N 17.86; found C 56.19, H 5.48, N 17.46.

4.1.2.2. 6-Nitro-1,2-dihydro-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5k). Yellow powder. Mp 264–265 °C. IR (KBr): 3385, 3166, 1690, 1618, 1530, 1329, 1140 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 6.02 (1H, t, J=1.7 Hz, CH), 6.83 (1H, d, J=8.8 Hz, ArH), 7.39 (1H, t, J=7.2 Hz, ArH), 7.42 (2H, t, J=7.2, 8.0 Hz, ArH), 7.49 (2H, d, J=8.0 Hz, ArH), 8.11 (1H, dd, J=2.8, 8.8 Hz, ArH), 8.44 (1H, d, J=2.8 Hz, ArH), 8.57 (1H, s, NH), 8.75 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 66.30, 112.64, 114.24, 124.18, 126.54 (2C), 128.65 (2C), 128.88, 128.97, 137.12, 141.09, 152.13, 161.28; MS (ESI): m/z (%)=270.1 (100) $[M+H]^+$; $C_{14}H_{11}N_3O_3$: calcd C 62.45, H 4.12, N 15.61; found C 62.28, H 3.80, N 15.25.

4.1.2.3. 6-Nitro-1,2-dihydro-2-*m*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5l). Yellow powder. Mp 294–296 °C. IR (KBr): 3321, 3191, 1685, 1618, 1532, 1324 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 6.25 (1H, s, CH), 6.89 (1H, d, J=8.8 Hz, ArH), 7.75 (1H, t, J=8.0 Hz, ArH), 7.94 (1H, d, J=8.0 Hz, ArH), 8.14 (1H, dd, J=2.8, 8.8 Hz, ArH), 8.26–8.27 (1H, m, J=1.6 Hz, ArH), 8.35 (1H, t, J=1.6 Hz, ArH), 8.44 (1H, d, J=2.8 Hz, ArH), 8.73 (1H, s, NH), 8.96 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.03, 112.69, 114.55, 121.38, 123.69, 124.16, 129.11, 130.45, 133.02, 137.50, 143.45, 147.80, 151.78, 161.19; MS (ESI): m/z (%)=315.4 (100) $[M+H]^+$; $C_{14}H_{10}N_4O_5$: calcd C 53.51, H 3.21, N 17.82; found C 53.22, H 3.27, N 17.72.

4.1.2.4. 6-Nitro-1,2-dihydro-2-*p*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5m). Yellow powder. Mp 263–265 °C. IR (KBr): 3350, 3084, 1690, 1621, 1522, 1330 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 6.21 (1H, s, CH), 6.87 (1H, d, J=8.8 Hz, ArH), 7.73 (2H, d, J=8.4 Hz, ArH), 8.13 (1H, dd, J=2.8, 8.8 Hz, ArH), 8.29 (2H, d, J=8.4 Hz, ArH), 8.43 (1H, d, J=2.8 Hz, ArH), 8.72 (1H, s, NH), 8.96 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.14, 112.63, 114.49, 123.92 (2C), 124.16, 127.80 (2C), 129.11, 137.44, 147.66, 148.29, 151.73, 161.09; MS (ESI): m/z (%)=315.4 (100) $[M+H]^+$; $C_{14}H_{10}N_4O_5$: calcd C 53.51, H 3.21, N 17.82; found C 53.33, H 3.31, N 17.46.

4.1.2.5. 6-Nitro-1,2-dihydro-2-*p*-methoxy-4-imino-4*H*-3,1-benzoxazine (5n). Yellow powder. Mp 242–243 °C. IR (KBr): 3385, 3162, 1660, 1620, 1512, 1309 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 3.75 (3H, s, CH_3), 5.97 (1H, s, CH), 6.82 (1H, d, J=8.8 Hz, ArH), 6.98 (2H, d, J=8.4 Hz, ArH), 7.39 (2H, d, J=8.4 Hz, ArH), 8.11 (1H, dd, J=2.8, 8.8 Hz, ArH), 8.43 (1H, d, J=2.8 Hz, ArH), 8.50 (1H, s, NH), 8.68 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 55.19, 65.91, 112.62, 113.90 (2C), 114.20, 124.16, 127.94 (2C), 128.93, 132.94, 136.99, 152.19, 159.67, 161.36; MS (ESI): m/z (%)=300.1 (100) $[M+H]^+$; $C_{15}H_{13}N_3O_4$: calcd C 60.19, H 4.38, N 14.04; found C 60.05, H 4.40, N 14.11.

4.1.2.6. 6-Nitro-1,2-dihydro-2-*p*-chlorophenyl-4-imino-4*H*-3,1-benzoxazine (5o). Yellow powder. Mp 263–265 °C. IR (KBr): 3366, 3180, 1692, 1615, 1492, 1328 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 6.06 (1H, s, CH), 6.84 (1H, d, J=8.8 Hz, ArH), 7.50 (4H, s, ArH), 8.13 (1H, dd, J=2.8, 8.8 Hz, ArH), 8.43 (1H, d, J=2.8 Hz, ArH), 8.59 (1H, s, NH), 8.80 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.49, 112.62, 114.32, 124.13, 128.45 (2C), 128.62 (2C), 128.99, 133.40, 137.23, 140.05, 151.96, 161.20; MS (ESI): m/z (%)=304.4 (100) $[M+H]^+$; $C_{14}H_{10}N_3O_3Cl$: calcd C 55.37, H 3.32, N 13.83; found C 55.59, H 3.62, N 13.44.

4.1.2.7. 7-Chloro-1,2-dihydro-2-propyl-4-imino-4*H*-3,1-benzoxazine (5p). Pale yellow powder. Mp 222–223 °C. IR (KBr): 3285, 3180, 2920, 1674, 1602, 1447 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.93 (3H, t, J=7.2 Hz, CH_3), 1.71–1.77 (2H, m, CH_2), 2.56–2.59 (2H, m, CH_2), 5.38 (1H, t, J=5.0 Hz, CH), 7.48 (1H, dd, J=2.0, 8.4 Hz, ArH), 7.64 (1H, d, J=2.0 Hz, ArH), 8.06 (1H, d, J=8.4 Hz, ArH), 8.19 (1H, s, NH), 8.38 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 13.40, 20.08, 36.31, 65.21, 125.89, 126.14, 127.73, 138.83, 150.02, 159.00, 161.14; MS (ESI): m/z (%)=225.1 (100) $[M+H]^+$; $C_{11}H_{13}N_2OCl$: calcd C 58.80, H 5.83, N 12.47; found C 59.20, H 5.48, N 12.21.

4.1.2.8. 7-Chloro-1,2-dihydro-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5q). Pale yellow powder. Mp 245–247 °C. IR (KBr): 3392, 3079, 1669, 1603 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.81 (1H, t, J=1.7 Hz, CH), 6.69 (1H, dd, J=2.0, 8.4 Hz, ArH), 6.80 (1H, d, J=2.0 Hz, ArH), 7.15 (1H, t, J=7.2 Hz, ArH), 7.23 (2H, t, J=7.2, 8.0 Hz, ArH), 7.27 (2H, d, J=8.0 Hz, ArH), 7.31 (1H, s, NH), 7.60 (1H, d, J=8.4 Hz, ArH), 8.41 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.23, 113.51, 113.61, 117.23, 121.76 (2C), 123.85 (2C), 129.38, 133.17, 137.90, 148.74, 159.12, 162.21; MS (ESI): m/z (%)=259.1 (100) $[M+H]^+$; $C_{14}H_{11}N_2OCl$: calcd C 64.99, H 4.29, N 10.83; found C 65.03, H 4.67, N 10.50.

4.1.2.9. 7-Chloro-1,2-dihydro-2-*m*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5r). Yellow powder. Mp 258–260 °C. IR (KBr): 3301, 3166, 1665, 1609, 1523, 1345 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 6.02 (1H, s, CH), 6.72 (1H, dd, J=1.8, 8.0 Hz, ArH), 6.83 (1H, d, J=1.8 Hz, ArH), 7.61 (2H, t, J=4.0, 4.0 Hz, ArH), 7.72 (1H, t, J=7.8, 7.8 Hz, ArH), 7.93 (1H, d, J=8.0 Hz, ArH), 8.21–8.23 (1H, m, J=1.6, 1.6 Hz, ArH), 8.35 (1H, s, NH), 8.66 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.09, 113.58, 113.63, 117.47, 121.48, 123.40, 129.42, 130.17, 133.18, 138.05, 143.94, 147.75, 148.22, 162.46; MS (ESI): m/z (%)=304.0 (100) $[M+H]^+$; $C_{14}H_{10}N_3O_3Cl$: calcd C 55.37, H 3.32, N 13.84; found C 55.76, H 3.35, N 13.75.

4.1.2.10. 7-Chloro-1,2-dihydro-2-*p*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5s). Yellow powder. Mp 243–244 °C. IR (KBr): 3355, 3282, 1660, 1609, 1521, 1351 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.99 (1H, s, CH), 6.70 (1H, dd, J=2.0, 8.4 Hz, ArH), 6.82 (1H, d, J=2.0 Hz, ArH), 7.60 (2H, d, J=8.4 Hz, ArH), 7.73 (2H, d, J=8.4 Hz, ArH), 8.26 (1H, s, NH), 8.27 (1H, d, J=8.4 Hz, ArH), 8.66 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.22, 113.59, 113.63, 117.43, 123.72 (2C), 127.95 (2C), 129.43, 138.09, 147.52, 148.20, 148.97, 162.42; MS (ESI): m/z (%)=304.0 (100) $[M+H]^+$; $C_{14}H_{10}N_3O_3Cl$: calcd C 55.37, H 3.32, N 13.84; found C 55.72, H 3.39, N 13.86.

4.1.2.11. 7-Chloro-1,2-dihydro-2-*p*-methoxy-4-imino-4*H*-3,1-benzoxazine (5t). Pale yellow powder. Mp 221–223 °C. IR (KBr): 3299, 3181, 1653, 1609, 1512 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 3.75 (3H, s, CH_3), 5.76 (1H, s, CH), 6.69 (1H, dd, J=2.0, 8.4 Hz, ArH), 6.78 (1H, d, J=2.0 Hz, ArH), 6.96 (2H, dd, J=1.6, 6.8 Hz, ArH), 7.29 (1H, s, NH), 7.41 (2H, dd, J=1.6, 6.8 Hz, ArH), 7.60 (1H, d, J=8.4 Hz, ArH), 8.32 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 55.21, 66.23, 113.45, 113.71, 113.76 (2C), 117.01, 128.17 (2C), 129.36, 133.17, 137.79, 148.94, 159.56, 162.84; MS (ESI): m/z (%)=289.0 (100) $[M+H]^+$; $C_{15}H_{13}N_2O_2Cl$: calcd C 62.40, H 4.54, N 9.70; found C 62.00, H 4.55, N 9.94.

4.1.2.12. 7-Chloro-1,2-dihydro-2-*p*-chlorophenyl-4-imino-4*H*-3,1-benzoxazine (5u). Yellow powder. Mp 242–244 °C. IR (KBr): 3251, 3166, 1649, 1609, 1484 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.85 (1H, s, CH), 6.70 (1H, dd, J=2.0, 8.4 Hz, ArH), 6.80 (1H, d, J=2.0 Hz, ArH), 7.43 (1H, s, NH), 7.47–7.52 (4H, m, J=2.4 Hz, ArH), 7.61 (1H, d, J=8.4 Hz, ArH), 8.48 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.69, 113.51, 113.59, 117.20, 128.42 (2C), 128.65 (2C), 129.36, 133.15, 137.93, 140.34, 148.56, 162.61; MS (ESI): m/z (%)=294.0 (100) $[M+H]^+$; $C_{14}H_{10}N_2OCl_2$: calcd C 57.36, H 3.44, N 9.56; found C 57.51, H 3.47, N 9.66.

4.1.2.13. 1,2-Dihydro-2-propyl-4-imino-4*H*-3,1-benzoxazine (5v). White powder. Mp 213–215 °C. IR (KBr): 3382, 3185, 2927, 1645, 1608, 1430 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 0.81 (3H, t, J=7.2 Hz, CH_3), 1.05–1.11 (2H, m, CH_2), 1.30–1.37 (2H, m, CH_2), 4.24 (1H, t, J=5.0 Hz, CH), 6.21 (1H, d, J=1.6 Hz, ArH), 6.42 (1H, s, NH), 6.51 (1H, d, J=1.6 Hz, ArH), 7.00–7.02 (1H, m, J=1.6, 1.2, 7.6 Hz, ArH), 7.37 (1H, dd, J=1.2, 7.6 Hz, ArH), 7.57 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 13.21, 18.21, 34.18, 66.45, 113.69, 114.19, 116.35, 127.16, 133.01, 146.89, 162.72; MS (ESI): m/z (%)=191.1 (100) $[M+H]^+$; $C_{11}H_{14}N_2O$: calcd C 69.44, H 7.42, N 14.73; found C 69.30, H 7.25, N 14.92.

4.1.2.14. 1,2-Dihydro-2-phenyl-4-imino-4*H*-3,1-benzoxazine (5w). White powder. Mp 224–226 °C. IR (KBr): 3370, 3177, 1678, 1608, 1472 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.71 (1H, t, J=1.7 Hz, CH), 6.77–6.79 (4H, m, J=8.0 Hz, ArH), 7.11 (1H, s, NH), 7.25 (1H, d, J=8.0 Hz, ArH), 7.31 (1H, t, J=8.0 Hz, ArH), 7.78 (3H, t, J=8.0 Hz, ArH), 8.28 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.64, 113.82, 114.30, 124.81, 127.45 (2C), 128.80 (2C), 128.88, 129.33, 133.38, 140.56, 147.23, 163.28; MS (ESI): m/z (%)=225.1 (100) $[M+H]^+$; $C_{14}H_{12}N_2O$: calcd C 74.98, H 5.39, N 12.49; found C 74.67, H 5.21, N 12.63.

4.1.2.15. 1,2-Dihydro-2-*m*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5x). Yellow powder. Mp 210–212 °C. IR (KBr): 3296, 3188, 1653, 1610, 1532, 1353 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.95 (1H, s, CH), 6.70 (1H, t, J=7.6 Hz, ArH), 6.79 (1H, d, J=8.0 Hz, ArH), 7.29 (1H, t, J=8.0 Hz, ArH), 7.35 (1H, s, NH), 7.62 (1H, dd, J=7.6 Hz, ArH), 7.70 (1H, t, J=7.6 Hz, ArH), 7.94 (1H, d, J=7.6 Hz, ArH), 8.21–8.22 (1H, m, J=1.4, 1.4 Hz, ArH), 8.36 (1H, t, J=1.8, 1.8 Hz, ArH), 8.53 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.20, 114.61, 114.97, 117.55, 121.59, 123.29, 127.43, 130.06, 133.39, 133.59, 144.32, 147.32, 147.73, 163.36; MS (ESI): m/z (%)=270.1 (100) $[M+H]^+$; $C_{14}H_{11}N_3O_3$: calcd C 62.45, H 4.12, N 15.61; found C 62.16, H 4.20, N 15.24.

4.1.2.16. 1,2-Dihydro-2-*p*-nitrophenyl-4-imino-4*H*-3,1-benzoxazine (5y). Yellow powder. Mp 198–200 °C. IR (KBr): 3389, 3282, 1647, 1615, 1520, 1349 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.91 (1H, s, CH), 6.68 (1H, t, J=7.6 Hz, ArH), 6.76 (1H, d, J=8.0 Hz, ArH), 7.26 (1H, t, J=7.6 Hz, ArH), 7.33 (1H, s, NH), 7.60 (1H, d, J=8.0 Hz, ArH), 7.73 (2H, d, J=8.4 Hz, ArH), 8.25 (2H, d, J=8.4 Hz, ArH), 8.51 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.76, 115.02, 115.38, 117.92, 124.02 (2C), 127.86, 128.48 (2C), 134.00, 147.68, 147.91, 149.81, 163.71; MS (ESI): m/z (%)=270.1 (100) $[M+H]^+$; $C_{14}H_{11}N_3O_3$: calcd C 62.45, H 4.12, N 15.61; found C 62.21, H 4.51, N 15.36.

4.1.2.17. 1,2-Dihydro-2-*p*-methoxy-4-imino-4*H*-3,1-benzoxazine (5z). White powder. Mp 255–257 °C. IR (KBr): 3269, 3171, 1678, 1602 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 3.86 (3H, s, CH_3), 5.67 (1H, s, CH), 6.42 (2H, dd, J=2.0, 7.6 Hz, ArH), 6.89–6.90 (1H, m, J=8.0 Hz, ArH), 7.04 (1H, s, NH), 7.15 (1H, d, J=8.0 Hz, ArH), 7.20–7.21 (1H, m, J=8.0 Hz, ArH), 7.36 (1H, dd, J=8.0 Hz, ArH), 7.45 (2H, dd, J=2.0, 7.6 Hz, ArH), 8.21 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 55.43, 65.36, 114.45, 114.71, 117.12 (2C), 117.69, 128.31 (2C), 128.75, 132.76, 133.79, 140.59, 147.56, 163.20; MS (ESI): m/z (%)=255.1 (100) $[M+H]^+$; $C_{15}H_{14}N_2O_2$: calcd C 70.85, H 5.55, N 11.02; found C 70.88, H 5.25, N 10.81.

4.1.2.18. 1,2-Dihydro-2-*p*-chlorophenyl-4-imino-4*H*-3,1-benzoxazine (5aa). White powder. Mp 227–228 °C. IR (KBr): 3325, 3188, 1658, 1609, 1483 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ_H: 5.78 (1H, s, CH), 6.67 (1H, t, J=8.0 Hz, ArH), 6.75 (1H, d, J=8.0 Hz, ArH), 7.15 (1H, s, NH), 7.25–7.27 (1H, m, J=8.0 Hz, ArH), 7.46–7.47 (2H, m, J=2.0, 6.4 Hz, ArH), 7.52 (2H, dd, J=2.0, 6.4 Hz, ArH), 7.62 (1H, dd, J=8.0 Hz, ArH), 8.34 (1H, s, =NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C: 65.79, 114.48, 114.97, 117.30, 127.39, 128.33, 128.34, 128.78 (2C), 132.99, 133.42, 140.70, 147.67, 163.50; MS (ESI): m/z (%)=259.1 (100) $[M+H]^+$; $C_{14}H_{11}N_2OCl$: calcd C 65.00, H 4.29, N 10.83; found C 65.38, H 4.36, N 10.88.

4.2. Crystallography

X-ray data for **3d** have been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 295187. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Crystal data for **3d**: $C_{12}H_{13}N_3O_3$; M=247.25, colorless block crystals, 0.50×0.50×0.50 mm, monoclinic, space group $C2/c$, a=19.206(4), b=8.7663(18), c=13.720(3) Å, β=90.03(3)°, V=2310.0(8) $Å^3$, Z=8, D_c=1.422 g cm^{-3}, $F(000)$=1040, μ (Mo Kα)=0.105 mm^{-1}. Intensity data were collected on a Rigaku Raxis RApid IP diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å) by using a $\omega-2\theta$ scan mode in the range of $2.55°<\theta<25.00°$. Out of 1973 unique reflections measured 1502 reflections with $I>2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97.[10] Nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located from a difference Fourier maps and refined without restraints. The final refinement was converged to R=0.0665 and wR=0.1947.

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